# REDOX POTENTIAL OF GLASS MELT IN A CONTINUOUS TECHNOLOGICAL PROCESS

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The effect of a combination of oppositely acting factors on the redox equilibrium of iron in glass and the diathermancy of glass melt is considered under the conditions of a continuous process of sheet-glass production.

One way of reducing the production cost of sheet glass for construction and technical purposes consists of changing over to less costly, usually local types of materials and increasing the quantity of utilized cullet. In some cases this is accompanied by an increase in the iron content in glass. The specifics of the electronic structure of iron determine its existence in the state of redox equilibrium:

$$Fe(II) \leftrightarrows Fe(III). \tag{1}$$

Despite the fact that ferric oxides are present in relatively small quantities (up to 0.2%) in the compositions of industrial non-tinted glasses, the relationship between the heterovalent forms of iron varies over a wide range. This ratio has a decisive effect on the glass-melting process and, consequently, on the technico-economical parameters of the furnace operation, since iron in the lower degree of oxidation Fe(II) contained in the glass melt decreases its diathermancy, which deteriorates the penetration of IR radiation in the depth of the glass melt and contributes to its substantial thermal and chemical inhomogeneity.

A substantial number of published papers analyzing the behavior of ferric oxide in silicate melts can be arbitrarily divided into two groups. The first ones study the effect of a certain technological factor on the equilibrium state (1). Such studies are usually related to melting insignificant volumes of binary or ternary silicate glasses in the laboratory under experimental production conditions. They include establishing the effect of the temperature-time process conditions, the composition of the gas medium above the melt, the redox potential (ROP) of the mixture, and the chemical composition of the glass on the redox equilibrium (1).

The effect of the melting temperature and the gas-medium composition above the melt on the valence state of iron is studied in [1]. It is established that as partial pressure of oxygen in the gas medium over the melt increases and the

melting temperature decreases, the equilibrium of the heterovalent iron forms is shifted toward a higher degree of oxidation.

The redox characteristics of raw materials serve for preliminary evaluation of the equilibrium state (1) in the glass melt based on variations in the estimated value of the batch ROP [1].

The effect of the glass composition on the equilibrium of the forms of iron is determined by the ratio of acid ($SiO_2$, $Al_2O_3$) and base ($Na_2O$, $K_2O$, MeO) oxides. The authors of various papers point to the shift of equilibrium (1) toward Fe(II) that takes place with an increasing share of acid oxides (acidity) in the glass. An increase in the base oxide content (increase in basicity) and, therefore, a decrease in the acidity of the glass reverts the direction of equilibrium (1).

The second group of studies is not numerous and is related to the practical implementation of the obtained results. The actual production process differs from the laboratory process in a great number of heterogeneous factors which together determine a specific ratio of the valent forms of iron in a glass melt. Therefore, it is essential to identify clearly and unambiguously the conditions of a continuous glass-melting process modifying the state of equilibrium (1).

It is interesting to carry out a comparative analysis and quantitatively estimate the behavior of $Fe_2O_3$ in industrial processes with different external factors. Since glass always contains iron in different degrees of oxidation, whose quantity can be easily determined using the standard methods [2], in studying the above-mentioned problem in accordance with the data in [1] we used the following expression:

$$d_{Fe(II)} = \frac{Fe(II) \cdot 100}{Fe(II) + Fe(III)},$$

where $d_{Fe(II)}$ is the part of bivalent iron in the glass, %, and Fe(II) and Fe(III) is the weight content of FeO and $Fe_2O_3$ converted to metal, %.

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The studies were performed in large regenerative glass-melting gas-heated furnaces with lateral flame direction. The design specifics of the furnaces are considered in [3, 4]. The chemical composition of glasses produced in the furnace systems, their melting regimes, the methods of introducing $Fe_2O$ in the glass composition, and also the glass melt parameters are given in Table 1. Furnaces 1 and 3 produced glass for construction purposes, and furnaces 2 and 4 produced glass for construction and technical purposes.

The glasses produced in furnaces 1 and 2 had similar chemical compositions; the overall content of high-melting (acid) oxides ($SiO_2 + Al_2O_3$) and fluxes ($Me_2O$ and $MeO$) was within the limits prescribed by the technological regulations. Both systems exhibited an increase in the overall iron content in glass converted to $Fe_2O_3$ when the materials were completely replaced with cullet (tank furnace 1, output 75 tons/day) and when the traditional materials were replaced by local raw materials [2] (tank furnace 2, output 160 tons/day). In the first case the overall $Fe_2O_3$ content increased from 0.118 to 0.178% (by 50.8%), and in the second case it increased from 0.073 to 0.180 % (by 146.5%). At the same time, the content of bivalent iron oxide, which changes the diathermancy of the glass melt, increased as well. In the first case the content of FeO converted to metal increased from 0.025 to 0.038% (by 52%), and in the second case from 0.0171 to 0.0481% (by 181.2%).

The increase in the total content of $Fe_2O_3$ intensified the glass tint from pale green to golden-brown in the first case, and to intense green in the second case. As the result, the melting capacity of tank furnaces 1 and 2 decreased, which was manifested in the impaired homogeneity of produced glass melt: in furnace 1 this index grew from 1.1 – 1.3 to 2.5 – 3.0°C. The diathermancy index of the glass melt evaluated according to the method in [5] decreased in both systems on the average by 18%.

The overall content of $Fe_2O_3$ in glass melt in furnaces 2 and 4 (output 140 and 180 tons/day, respectively) increased due to the substitution of the types of materials, which was accompanied by a modification in the basic composition of the glass. The glasses produced in these furnaces had significant differences in the content of high-melting and low-melting oxides. The actual increase in the $Fe_2O_3$ content on a variation in the specified factors was 18.3% (from 0.060 to 0.071%) in system 3 and 13.1% (from 0.122 to 0.138%) in system 4. At the same time, the FeO content in glasses in furnace 3 increased by 44.3% (from 0.0124 to 0.0179% converted to metal), and in system 4 by 25% (from 0.027 to 0.034%).

An integrated analysis of the operation of the glass-melting furnaces suggests a number of common features. First, in all cases an increase in the overall content of $Fe_2O_3$ and FeO in the glass results in decreased diathermancy of the melt and its deteriorated homogeneity. The maximum inhomogeneity of 3°C was registered in tank furnace 1 on introducing 100% cullet. In other systems, the glass-melt inhomogeneity index

after an increase in the Fe(II) content was not as high (up to 1.8 – 2.0°C).

The part of bivalent iron in the glass did not change on introducing 100% cullet (tank furnace 1). The same parameter for tank furnace 2 increased from 33.5 to 38.1% (by 4.6%), and for tank furnace 3 it increased from 29.5 to 37.5% (by 8%). The changes occurred in furnace 2 on introducing new types of materials, and in furnace 3 on the simultaneous modification of the chemical composition of glass and the type of materials.

In the first two cases (furnaces 1 and 2), the basic chemical composition of the manufactured glass did not vary (Table 1). This fact is also corroborated by the ratio of the sum of the base oxides to the sum of the acid oxides:

$$\frac{Me_2 + MeO}{SiO_2 + Al_2O_3}. \tag{2}$$

This sum was within the limits of 0.34 – 0.35. For a virtually equal content of ferric oxide (0.178 and 0.180%, respectively, for furnaces 1 and 2), the equilibrium Fe(II) ⇆ Fe(III) in system 2 was shifted to the left (an increase in the content of Fe(II) by 4.6%: from 33.5 to 38.1%), whereas the content of Fe(II) in system 1 remained constant. Therefore, the introduction of new types of materials accompanied by a decrease in the batch ROP from 15.45 to 13.17 (furnace 2) resulted in an increased ROP of the glass melt, which shifted equilibrium (1) to the left. Contrary to this, although the complete replacement of virgin material by cullet (furnace 1) and the weakly reducing conditions of glass melting (0.2% CO in the atmosphere of this furnace) modified the diathermancy of the melt, they did not affect the ROP of the glass melt, which determined the virtually constant content of Fe(II): 30.1 – 30.4%.

The effect of all the contradictory factors on iron was studied in tank furnaces 2 and 4. Monitoring of the process in system 3 revealed an increased content of low-melting (base) oxides and a simultaneous decrease in high-melting (acid) oxides. Ratio (2) grew from 0.32 to 0.35 on simultaneous replacement of the type of materials (the batch ROP decreases from 11.72 to 9.09). The actual absolute increment of $Fe_2O_3$ in the glass amounted to 0.01%. However, the effect of two opposite factors on the iron-bearing melt (the increase in glass basicity and the increased batch ROP) shifted the equilibrium Fe(II) ⇆ Fe(III) to the left (the content of Fe(II) grew by 8%: from 29.5 to 37.5%), which is evidence of the intensification of the reducing properties of the melt.

The process in furnace 4 revealed an increased content of low-melting oxides and a decreased amount of high-melting oxides, which determined the increased basicity of the glass: ratio (2) increased from 0.25 to 0.39. This is the maximum value of this parameter in all four cases considered. The same as in furnace 3, the variation in the basic composition of the glass was accompanied by simultaneous replacement of raw materials. The ROP of the batch in this case increased

**TABLE 1**

| Parameter | Tank furnace 1 | | Tank furnace 2 | | Tank furnace 3 | | Tank furnace 4 | |
|---|---|---|---|---|---|---|---|---|
| | Cullet, traditional material | 100% cullet | Cullet, traditional material | Cullet, new types of materials | Cullet, traditional material | Cullet, new types of materials | Cullet, traditional material | Cullet, new types of materials |
| Design capacity, tons/day | 75 | 75 | 160 | 160 | 140 | 140 | 80 | 80 |
| Basic glass composition from analysis: | | | | | | | | |
| $SiO_2 + Al_2O_3$ | 73.77 | 73.44 | 73.60 | 73.80 | 74.63 | 73.30 | 73.08 | 70.94 |
| $Me_2O + MeO$ | 25.66 | 25.87 | 25.93 | 25.71 | 24.38 | 26.02 | 26.57 | 27.88 |
| Ratio $\dfrac{Me_2 + MeO}{SiO_2 + Al_2O_3}$ | 0.34 | 0.35 | 0.35 | 0.35 | 0.32 | 0.35 | 0.36 | 0.39 |
| Batch ROP | 6.80 | – | 15.45 | 13.17 | 11.72 | 9.09 | 11.21 | 11.66 |
| Impurity composition of glass, %: | | | | | | | | |
| $Fe_2O_3$ | 0.1180 | 0.1780 | 0.0730 | 0.1800 | 0.0600 | 0.0710 | 0.1220 | 0.1380 |
| $Fe_{tot} = Fe(II) + Fe(III)$ | 0.0830 | 0.1250 | 0.0510 | 0.1260 | 0.0420 | 0.0470 | 0.0820 | 0.0920 |
| $Fe(II)$ | 0.0250 | 0.0380 | 0.0171 | 0.0481 | 0.0124 | 0.0179 | 0.0270 | 0.0340 |
| $d_{Fe(II)}$ | 30.1 | 30.4 | 33.5 | 38.1 | 29.5 | 37.5 | 32.9 | 36.9 |
| Maximum melting temperature, °C | 1500 | 1515 | 1520 | 1560 | 1470 | 1510 | 1510 | 1530 |
| Content of CO by volume, % | 0.0 | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Diathermancy index | 6.7 | 5.6 | 6.9 | 5.7 | Not determined | | | |
| Homogeneity, °C | 1.1 – 1.3 | 2.5 – 3.0 | 1.1 – 1.3 | 1.8 | 1.5 – 2.0 | 1.5 – 2.0 | 1.8 | 1.9 |

by 0.45, which points to a slight increase in its oxidizing capacity. However, the registered increase in the total content of $Fe_2O_3$ in the glass by 0.016% (from 0.122 to 0.138%), which caused an increase in the amount of FeO (from 0.017 to 0.034% converted to metal) combined with uncontrollable reducing impurities present in the new material, resulted in the increased ROP of the glass melt in furnace 4. Its consequence was a shift to the left in equilibrium (1) (the content of Fe(II) increased from 32.9 to 36.9).

Thus, in producing sheet glass for construction and technical purposes one should take into account the combined effect of various technological factors and external conditions which have opposite effects on the glass melt ROP. The actual modification of the ROP can be indirectly estimated by fluctuations in the content of bivalent iron in the glass.

The effect of a combination of opposite factors, such as increased $Fe_2O_3$ content in glass, increased basicity of the basic glass composition (a decrease in acidity), and increase in the batch ROP result in an increased ROP of the glass melt, which determines the increase in the share of bivalent iron and its absolute content in the glass. This causes a decrease in the diathermancy of the melt, increases the emission of heat into the gas space of the tank furnace, and deter-

mines the increased thermal stress in the main roof of the furnace as well as the possible shortening of the service life of the tank furnace.

With the purpose of improving the glass-melting process, the ROP of the batch in systems 2 and 3 was modified accordingly, and a new melting catalyst was introduced.

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